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Preliminary communication

DIRECTED SYNTHESIS OF MIXED METAL CHALCOGENIDE CLUSTERS: OXIDATIVE ADDITIONS OF $Fe_2(\mu_2\text{-}E_2)(CO)_6$ (E = S, Se, Te)*

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Summary

The reaction of $Fe_2(\mu_2\text{-}E_2)(CO)_6$ with $M(PPh_3)_2(C_2H_4)$ affords quantitative yields of $(CO)_6Fe_2(\mu_3\text{-}E)_2M(PPh_3)_2$ (E = S, Se, Te; M = Pt, Pd), which were characterized by analytical data, molecular weight measurements, IR, and heteronuclear NMR.

Polynuclear metal complexes which contain chalcogenides in their framework are not unusual but have become the subject of renewed scrutiny due to their apparent involvement in catalysis in biochemical and industrial applications, viz. Mo—Fe—S [1—3] in nitrogenase and $Rh_{17}(CO)_{32}S_2{}^{3-}$ [4,5] in the synthesis of alcohols from sulfur-poisoned synthesis gas. There exist few reliable and predictable high-yield synthetic routes to such polynuclear metal chalcogenides, especially the more interesting heterometallic variety. Recent reports of the reactivity of dichalcogenide ligands, e.g. S_2, have demonstrated in the case of $Fe_2(\mu_2\text{-}S_2)(CO)_6$ its similarity to an organic disulfide in its reductive and photochemical reactions with organic reagents [6—8]. Pursuant to the dimetallodisulfide analogy we have sought (and found) reactivity patterns akin to the oxidative addition of organic disulfides with low valent metal ions which is known to afford dimercaptides [9].

Treatment of $Fe_2(\mu_2\text{-}S_2)(CO)_6$ [10] with $Pt(PPh_3)_2C_2H_4$ (I) (1 equiv.) in benzene (25°C) results in the rapid (< 10 min) and quantitative (by TLC on silica gel) formation of the trinuclear cluster $(CO)_6Fe_2(\mu_3\text{-}S)_2Pt(PPh_3)_2$ (II)** (eq. 1). Compound II isolated as deep red crystals from hexane in 85% yield. Compound II was also prepared from the recently reported [6]

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*This work was presented in part at the 179th ACS national meeting, Houston, Texas; March, 1980; see abstract INOR-93.

**Unless otherwise noted, all new compounds gave satisfactory elemental analysis (C,H,Fe,E,P), parent ions in their field desorption mass spectra, ^{31}P NMR, and IR spectra consistent with the proposed formulations.

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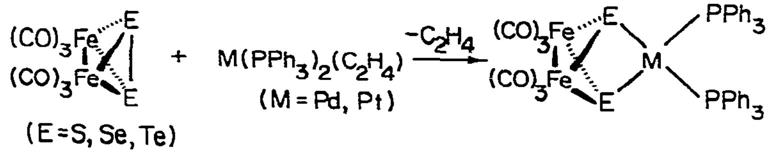

(1)

$Fe_2(\mu_2\text{-}S_2)(CO)_6{}^{2-}$ (prepared by the KH reduction of $Fe_2(\mu_2\text{-}S_2)(CO)_6$) albeit in only 14% yield (eq. 2).

$$Fe_2(\mu_2\text{-}S_2)(CO)_6{}^{2-} + cis\text{-}PtCl_2(PPh_3)_2 \rightarrow (CO)_6Fe_2(\mu_3\text{-}S)_2Pt(PPh_3)_2 \qquad (2)$$

The infrared spectrum of II in hexane shows four strong carbonyl absorptions (2047, 2002, 1969, 1953 cm^{-1}) consistent with its C_{2v} symmetry, while the $^{31}P\{^1H\}$NMR measurement demonstrates that the phosphines are equivalent and bound to platinum, $^1J(^{195}Pt, ^{31}P)$ 2790 Hz. The spectroscopic and analytical (C, H, Fe, S, P) data are supported by field desorption mass spectrometry where the molecular ion is observed at $m/e = 1063$ (100%) as expected for $(CO)_6{}^{56}Fe_2(\mu_3\text{-}S)_2{}^{195}Pt(PPh_3)_2$. Confirmatory structural information derives from spectroscopic examination of $(CO)_5(PPh_3)Fe_2(\mu_3\text{-}S)_2Pt(PPh_3)_2$ which we prepared from the reaction of I with $Fe_2(\mu_2\text{-}S_2)(CO)_5(PPh_3)$ [11]*. The $^{31}P\{^1H\}$of this latter complex shows signals for the phosphines bound to the iron and platinum in a 1/2 ratio ($^1J(^{195}Pt, ^{31}P)$ 2826 Hz, $^3J(^{195}Pt, ^{31}P)$ 84 Hz, $^4J(^{31}P, ^{31}P)$ 7 Hz). In a similar manner the palladium derivative $(CO)_6Fe_2(\mu_3\text{-}S)_2Pd(PPh_3)_2$ (III), was also prepared starting from $Pd(PPh_3)_2(C_2H_4)$ again in quantitative conversion under ambient conditions. The infrared spectrum of III is nearly identival to that of II.

The reaction can also be applied to other dichalcogenide complexes. For instance $(CO)_6Fe_2(\mu_3\text{-}Se)_2Pt(PPh_3)_2$ (IV) was prepared in quantitative yield from $Fe_2(\mu_2\text{-}Se_2)(CO)_6$ [10] and I. In addition to the usual characterization, the Fourier transform $^{31}P\{^1H\}$NMR reveals the ^{77}Se coupling, $^2J(^{77}Se, ^{31}P)$ 24 Hz, in both the center line and ^{195}Pt satellites. For comparison, Ph_2Se_2 also reacts with I, affording $cis\text{-}Pt(SePh)_2(PPh_3)_2$ which by $^{31}P\{^1H\}$ NMR has a $^2J(^{77}Se, ^{31}P)$ of 45 Hz.

$Fe_2(\mu_2\text{-}Te_2)(CO)_6$ is not a known compound. Indeed, reaction of K_2TeO_3 with $Fe(CO)_5|OH^-$ using the Hieber method [9] affords a good yield of the known black $Fe_3(\mu_3\text{-}Te)_2(CO)_9$. Fractional sublimation (0.1 mmHg, 45°C, 36 h) of this crude product does, however, afford a small quantity (< 1% of total) of a black mixture which by IR appears to be comprised of both $Fe_3(\mu_3\text{-}Te)_2(CO)_9$, $\nu(CO)$ (hexane) 2045 s, 2025 s, 2004 s cm^{-1} and the previously unknown $Fe_2(\mu_2\text{-}Te_2)(CO)_6$, $\nu(CO)$ (hexane) 2067 m, 2028 s, 1995 s cm^{-1}. As the presumed $Fe_2(\mu_2\text{-}Te_2)(CO)_6$ could not be purified further by adsorption chromatography, the mixture was treated directly with I (C_6H_6, 15 min, 25°C), affording a chromatographically separable mixture of unreacted $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ and the desired $(CO)_6Fe_2(\mu_3\text{-}Te)_2\text{-}Pt(PPh_3)_2$*. In addition to substantiating the existence of the unprecedented coordinated Te_2 moiety this trapping reaction illustrates the efficiency of

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*These compounds were purified chromatographically and characterized by IR, ^{31}P NMR, and in the case of $(CO)_6Fe_2(\mu_3\text{-}Te)_2Pt(PPh_3)_2$, by field desorption mass spectrometry.

the oxidative addition processes involving dimetallodichalcogenides. Interestingly, I does not react with Ph_2Te_2 after 48 h (25°C). Thus it appears that at least in this instance the dimetallodichalcogenide is significantly more reactive than the corresponding diorganodichalcogenide.

Acknowledgments

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Note added in proof: Since submission of this work, Seyferth and co-workers have reported similar results: see D. Seyferth, R.S. Henderson and M.K. Gallagher, J. Organometal. Chem., 193 (1980) C75.